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Comparison of Properties and Structure of Zinc Chelates of 8-Hydroxyquinoline, 8-Mercaptoquinoline, and 8-Selenoquinoline

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The properties and the structure of zinc chelates of 8-hydroxyquinoline, 8-mercaptoquinoline, and 8-selenoquinoline are compared and discussed on the basis of the results of thermogravimetric and thermal differential analysis, X-ray diffraction and ultraviolet and visible absorption spectra in chloroform. It is concluded that 1 : 2 zinc chelates of 8HQ, 8MQ, and 8SeQ have the tetrahedral structure and that Zn-8HQ adducts the basic ligands such as water and pyridine molecules accompanying the change of the structure from tetrahedral to distored octahedral. Otherwise, Zn-8MQ and Zn-8SeQ have no ability to form the adduct.

It is interesting to know how to change the properties and the structure of the metal chelates when one donor atom of its ligand is replaced by another atom. 8-Mercaptoquinoline (abbrivated as 8MQ) and 8-selenoquinoline (8SeQ) are the ligands which the donor oxygen atom of 8-hydroxyquinoline (8HQ) is replaced by sulfur and selenium atoms respectively which belong to VI_a group. In this paper, 8HQ, 8MQ, and 8SeQ are taken up as the ligands and the properties and the structures of zinc chelates of these three ligands are studied and compared.

EXPERIMENTAL

Reagents

Sodium Salts of 8MQ and 8SeQ. The sodium salt of 8MQ anhydride was prepared by the method of Nakamura and Sekido.[1] 8SeQ was synthesized by the modified method of Sekido, Fernando, and Freiser,[2] and its sodium salt monohydrate was prepared by the method of Sekido and Fujiwara.[3]

8HQ. The reagent grade 8HQ was crystallized from absolute ethanol for three times.

All reagents including buffer components were of analytical reagent grade.

Formation of Zn-8HQ. 8HQ (3.0 g.) dissolved in ethanol (80 ml.) was slowly added with stirring to 0.1 M zinc nitrate solution (100 ml.) buffered with acetic acid and sodium acetate at room temperature. The formed precipitate was filtered and washed with hot water at 40°C for several times and dried in air on a filter paper.

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Formation of Zn-8MQ and Zn-8SeQ. The sodium salt of 8MQ (1.3–1.5 g.) was dissolved in water (100 ml.) and the pH of the solution was adjusted to 2.1 with hydrochloric acid at room temperature under nitrogen gas. The formed precipitate was filtered and washed with water for several times and dried in air on a filter paper. The reagent solution was made up fresh each time the precipitate was formed. Zn-8SeQ was prepared by the same method of Zn-8MQ.

Apparatus and Measurements

Thermogravimetric and Differential Thermal Analysis. The thermogravimetric analysis (TGA) curves and the differential thermal analysis (DTA) curves were recorded at the same time with a Rigaku TG-DTA unit. The powdered sample (10 mg.) was weighed out in a Pt-Rh dish and the temperature was raised on heating rate of 10°C/min. from room temperature to 800°C. α-Alumina powder was used as the inert material for DTA measurement.

X-ray Diffraction. X-ray diffraction patterns were obtained with a Rigaku X-ray diffractometer using nickel-filtered Cu K_α (λ=1.54 Å).

Ultraviolet and Visible Absorption Spectra. The absorption spectra of the zinc chelates in chloroform solution were measured in the range of 300 to 450 nm with Hitachi-124 spectrophotometer using 1 mm and 10 mm cells.

RESULTS AND DISCUSSION

TGA and DTA Curves of Zn-8HQ, Zn-8MQ, and Zn-8SeQ Chelates.

The TGA and DTA curves of the air drying samples of Zn-8HQ, Zn-8MQ, and Zn-8SeQ are shown in Figs. 1 and 2, respectively. Zn-8MQ and Zn-8SeQ are stable against heating in the range of room temperature to 200°C for Zn-8MQ and Zn-8SeQ, but for Zn-8HQ, the weight loss of 9.2% corresponding to releasing of two molecules of water for $Zn(C_9H_6ON)_2 2H_2O$ is observed in the range of 100 to 160°C on the TGA curve *a* in Fig. 1 and a endothermic peak corresponding to this weight loss is found on the DTA

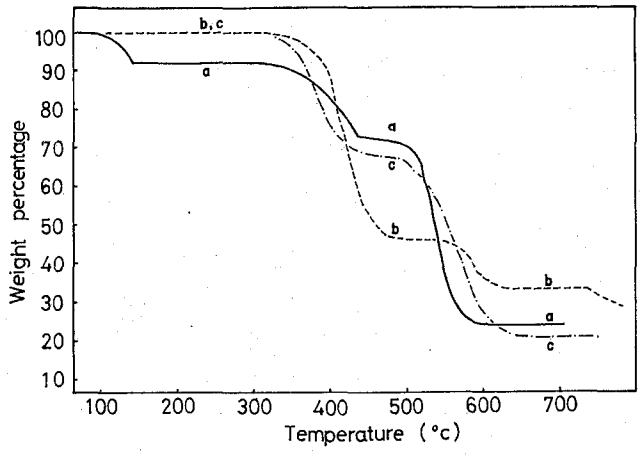

Fig. 1. Thermogravimetric analysis curves of Zn-8HQ, Zn-8MQ, and Zn-8SeQ chelates. *a*: Zn-8HQ (——), *b*: Zn-8MQ (----), *c*: Zn-8SeQ (—·—).

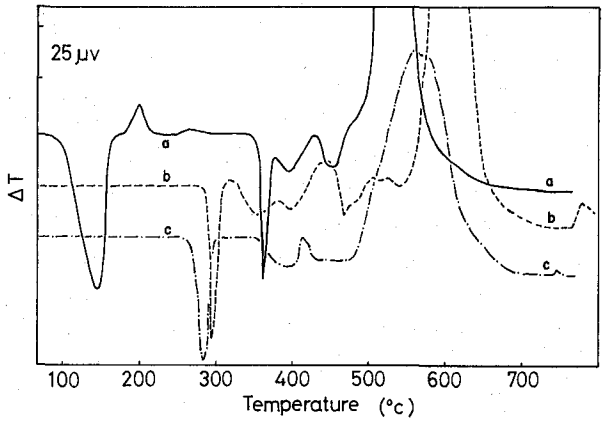

Fig. 2. Differential thermal analysis curves of Zn-8HQ, Zn-8MQ, and Zn-8SeQ chelates. *a*: Zn-8HQ (——), *b*: Zn-8MQ (----), *c*: Zn-8SeQ (—·—).

curve *a* in Fig. 2. Moreover, for Zn-8HQ, it is found that a weak exothermic peak accompanying no weight loss is found at 200°C. The TGA and DTA curves above 200°C for three compounds, especially for Zn-8MQ and Zn-8SeQ, are similar. The endothermic peaks at 290°C for Zn-8SeQ, 295°C for Zn-8MQ and 365°C for Zn-8HQ correspond to the melting for these compounds. After melting these three compounds seem to lose the weight on the two steps as seen in Fig. 1. For Zn-8HQ and Zn-8SeQ, the first step can be regarded as the release of one ligand molecule or its fragment and second step can be done as the oxidative decomposition of 1 : 1 zinc chelate accompanied with a large exothermic peak. However, for Zn-8MQ, the weight loss percent on the first step, 55%, is very larger than those for Zn-8HQ and Zn-8SeQ. Probably, in the case of Zn-8MQ, the weight loss by the decomposition of 8,8′-diquinolyldisulfide which is formed by further decomposition of the residual 1 : 1 Zn-8MQ chelate will be included.

It is interesting that there is a linear relationship between the melting points of three

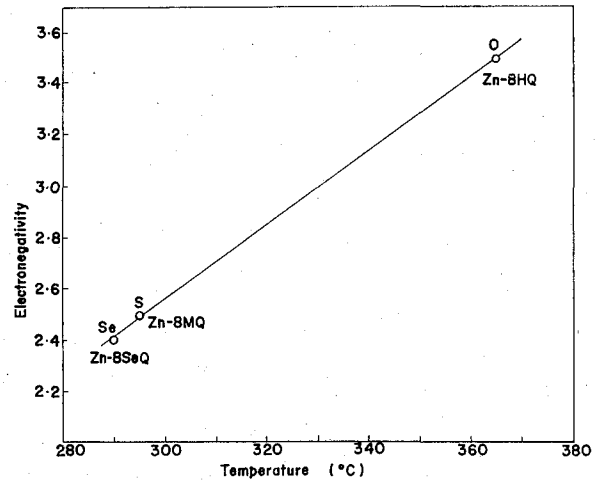

Fig. 3. Plots of electronegativity (O, S, and Se) *vs.* melting point of Zn-8HQ, Zn-8MQ, and Zn-8SeQ.

compounds and their electronegativities of the ligand atoms, oxygen, sulfur, and selenium, as shown in Fig. 3.

The ionic bond character for Zn-O bond may be greater than that for Zn-S or Zn–Se bond, and the zinc atom in the 1 : 2 chelate of Zn-8HQ will attract two molecules of water in aqueous solution and the dihydrate of 1 : 2 Zn-8HQ chelate which has the distorted octahedral structure[4,5] will be precipitated. Accordingly, for the anhydride of Zn-8HQ which the two molecules of water were released on heating, the residual force will be served as the intermolecular force of Zn-8HQ molecule, although its structure changes to tetrahedral to hold energetically stable state. On the other hand, Zn-S and Zn-Se bonds may have more covalent bond character than for Zn-O bond and may have the ability to form the back donated π-bond so that Zn-8MQ and Zn-8SeQ form no adduct, that is, will hardly have ionic residual intermolecular force. Therefore, the melting point for Zn-8HQ may be higher than those for Zn-8MQ and Zn-8SeQ.

A weak exothermic peak at 200°C appeared for Zn-8HQ but not for Zn-8MQ and Zn-8SeQ will be attributed to the rearrangement of the crystal lattice to the anhydride having the tetrahedral configuration[6] from the dihydrate having the distorted octahedral one.

X-ray Diffraction for Zn-8HQ, Zn-8MQ, and Zn-8SeQ Chelates

The X-ray diffraction patterns for Zn-8HQ air drying sample and its heated samples are shown in Fig. 4. The pattern *a* in Fig. 4 indicates that the dihydrate of Zn-8HQ is a good crystalline state and the lattice spacings calculated from this diffraction pattern

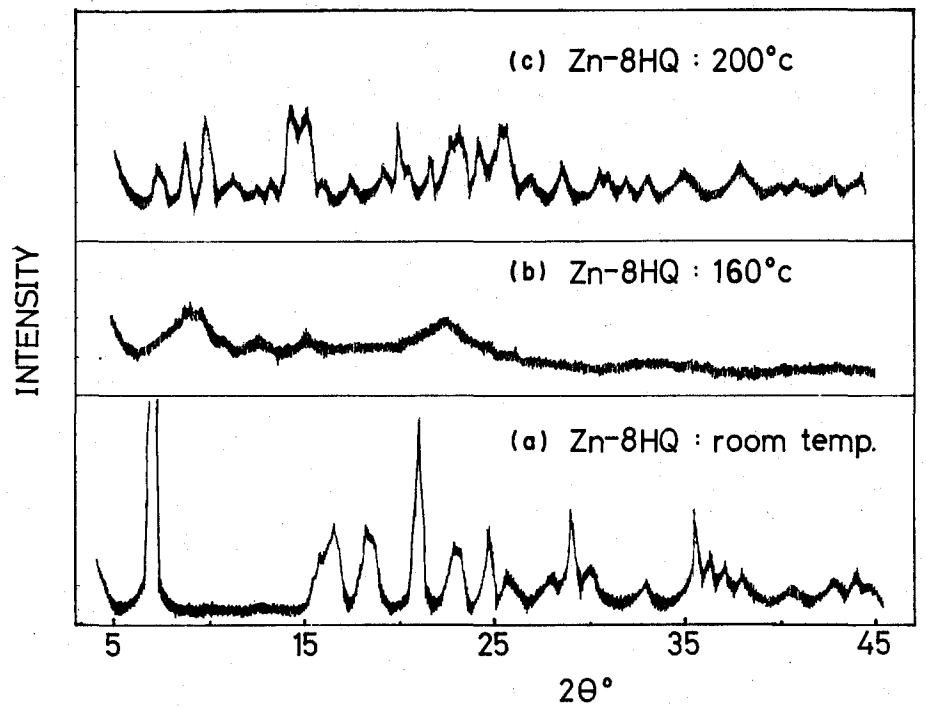

Fig. 4. X-ray diffraction patterns of Zn-8HQ chelate. *a*: Zn-8HQ·2H_2O, *b*: Zn-8HQ (160°C), *c*: Zn-8HQ (200°C).

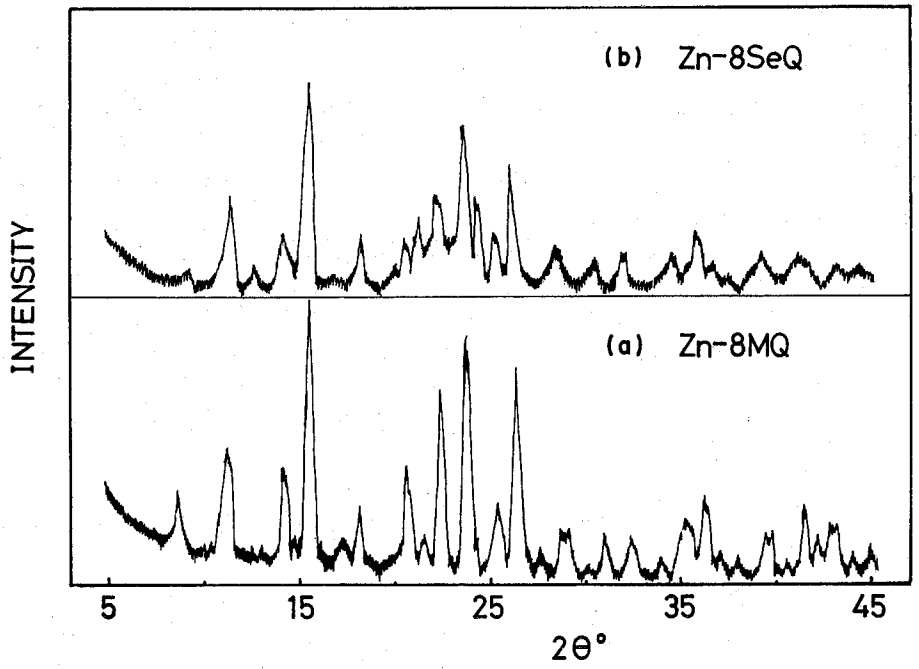

Fig. 5. X-ray diffraction patterns of Zn-8MQ and Zn-8SeQ chelates.
a: Zn-8MQ, *b*: Zn-8SeQ.

Table I. X-ray Diffraction Data of Zn-8HQ, Zn-8MQ, and Zn-8SeQ.

Zn-8HQ·2H$_2$O		Zn-8HQ		Zn-8MQ		Zn-8SeQ	
d (Å)	I	*d* (Å)	I	*d* (Å)	I	*d* (Å)	I
12.81	100						
		10.16	78	10.21	16		
		9.31	72				
		9.07	76	7.87	48	7.92	46
		6.28	91	6.24	40	6.30	23
5.51	13	5.85	100	5.72	100	5.81	100
5.39	19	5.04	20	4.81	25	4.90	27
4.86	21	4.62	22				
4.76	15	4.45	83				
4.23	45	4.31	35	4.07	42		
		4.11	45	4.14	15	4.15	34
		3.93	43	3.99	69	4.00	46
3.85	13	3.84	65	3.75	88	3.81	60
3.62	18	3.66	54	3.51	28	3.69	43
		3.53	52	3.38	75	3.43	52
				3.10	16		
2.53	23					2.51	24

coincide to those calculated using the cell constants obtained from the results of X-ray crystalographic analysis of $Zn(C_9H_6ON)_22H_2O$. When the dihydrate is heated to 160°C with the heating rate of 10°C/min., the pattern changes to the amorphous one (pattern *b*). On the heating at 200°C, new peaks appear, which indicates that the crystal of the anhydride begins to grow (pattern *c*). It is found that the peaks become stronger on heating at 200°C for two hours. The X-ray diffraction patterns for the air drying Zn-8MQ as well as Zn-8SeQ are same as for those on heating at 130°C and 200°C for 2 hours. Zn-8MQ, Zn-8SeQ, and the anhydride of Zn-8HQ give the similar X-ray diffraction patterns, especially for Zn-8MQ and Zn-8SeQ as shown in Fig. 5 *a* and *b*. The values of lattice spacing, *d* for Zn-8MQ and Zn-8SeQ and those intensities correspond as seen in Table I. The fact that the values of *d* for Zn-8SeQ are a little greater than for corresponding those for Zn-8MQ can be attributed to a little more bulky molecule of Zn-8SeQ than that of Zn-8MQ because of the larger radius of selenium atom than that of sulfur atom.

Ultraviolet and Visible Absorption Spectra for Zn-8HQ, Zn-8MQ, and Zn-8SeQ Chelates

The low energy transition band appeared at 412 nm for Cu-8HQ chelate in chloroform has been assigned as ^1L_a transition mixed with the charge transfer from copper to the ligand.[7] The absorption spectra appeared in the range of 380 to 430 nm for Zn-8HQ in various organic solvents will be also assigned as ^1L_a band mixed with a charge transfer as well as for Cu-8HQ chelate. As shown in Table II, the ^1L_a band shifts to longer wavelengths in the order of Zn-8HQ<Zn-8MQ<Zn-8SeQ in each organic solvent, carbon tetrachloride, benzene, and chloroform.

Absorption Spectra of Zn-8HQ, Zn-8MQ, and Zn-8SeQ Chelates in Chloroform Solution

The absorption spectra of the anhydride of Zn-8HQ in the chloroform solutions are shown in Fig. 6. The ^1L_a band of Zn-8HQ in the chloroform desiccated with phosphorous pentoxide locates at 375 nm but that in the chloroform desiccated with sodium sulfate anhydride shifts to longer wavelength, 380 nm, and their molar extinction coefficient becomes also large from 3.6×10^3 to 4.1×10^3. When small amounts of pyridine is contained in chloroform, the band shifts long wavelength (397 nm) and the molar extinction coefficient becomes also large (4.4×10^3). On the other hand, the ^1L_a band for Zn-8MQ as well as for Zn-8SeQ is same in chloroform desiccated with either sodium

Table II. ^1L_a Absorption Band of Zn-8HQ, Zn-8MQ, and Zn-8SeQ in Various Organic Solvents

Solvent	Zn-8HQ (nm)	Zn-8MQ (nm)	Zn-8SeQ (nm)
Carbon tetrachloride	386	420	430
Benzene	383	413	423
Chloroform*	380	403	412

* desiccated with sodium sulfate anhydride.

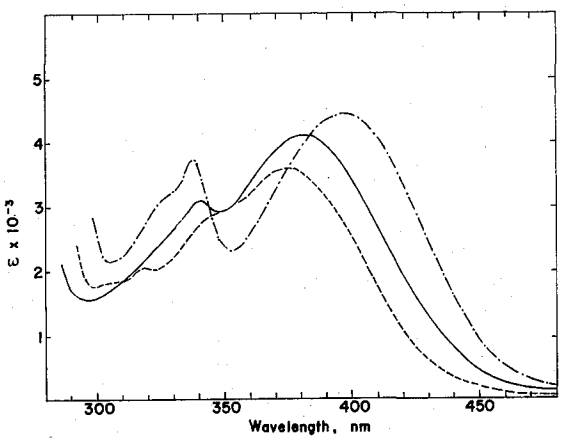

Fig. 6. Ultraviolet and visible absorption spectra of Zn-8HQ in chloroform solutions. ——: in chloroform desiccated with sodium sulfate anhydride, ----: in chloroform desiccated with phosphorous pentoxide, —·—: in chloroform containing 2.0×10^{-2} M pyridine.

sulfate anhydride or phosphorous pentoxide and is also same in chloroform containing pyridine as shown in Fig. 7. Moreover, ^1L_a bands for Zn-8MQ and Zn-8SeQ are similar to that for Zn-8HQ in the chloroform desiccated with phosphorous pentoxide. Even if small amounts of water or pyridine is contained in chloroform, Zn-8MQ and Zn-8SeQ do not coordinate water or pyridine, therefore, the tetrahedral structure of these chelates will be maintained. On the other hand, although the anhydride of Zn-8HQ may be tetrahedral in the chloroform completely desiccated with phosphorous pentoxide, it coordinates small amounts of water being contained in chloroform incompletely desiccated with sodium sulfate anhydride and its structure will change from tetrahedral to

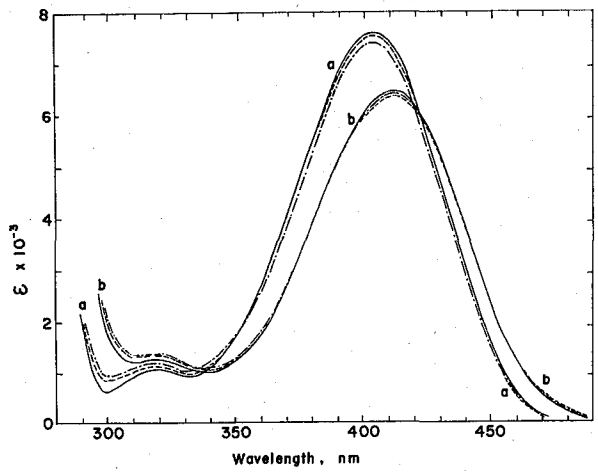

Fig. 7. Ultraviolet and visible absorption spectra of Zn-8MQ and Zn-8SeQ chelates in chloroform solutions. Curve *a* group: Zn-8MQ, curve *b* group: Zn-8SeQ. ——: in chloroform saturated with water, ----: in chloroform desiccated with phosphorous pentoxide or sodium sulfate anhydride, —·—: in chloroform containing 2×10^{-2} M pyridine.

distorted octahedral structure. The solubility of the dihydrate of Zn-8HQ is so poor in both organic solvents and water that the dihydrate will be precipitated on standing for long time. Consequently, the band in chloroform desiccated with sodium sulfate anhydride may be ascribed by the distorted octahedral structure which coordinates two molecules of water above and below of zinc atom of 1 : 2 trans-planar Zn-8HQ molecule. Similarly, the band of Zn-8HQ in the chloroform containing pyridine will be ascribed to the Zn-8HQ chelate adducted with pyridine molecules which is stable in chloroform.

CONCLUSIONS

The results of TGA and DTA, X-ray diffraction and the absorption spectra in chloroform indicate that 8HQ, 8MQ, and 8SeQ having oxygen, sulfur, and selenium atoms as one of the donor atoms respectively, form the tetrahedral 1 : 2 chelate with zinc atom. Further, for Zn-8HQ, the zinc atom has the ability to adduct the basic ligands such as water and pyridine molecules and its structure varies distorted octahedral but Zn-8MQ and Zn-8SeQ chelates have no ability to form the adduct, so that their structures may be maintained to tetrahedral.

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